A RELATION BETWEEN VELOCITY OF SOUND IN LIQUIDS AND MOLECULAR VOLUME

By M. RAMA RAO, M.Sc.
Department of Physics, University of Mysore, Bangalore

(Received for publication, March 15, 1940)

ABSTRACT. The relation $v^{\frac{1}{3}} . V = R$ between the velocity of sound in liquids (v) and molecular volume (V) holds good in a large number of liquids. Combining this with the expression for the energy of a vibrating molecule and Debye's expression for the frequency of a vibrating molecule, it is shown that the energy of a vibrating molecule, is proportional to its frequency of vibration. An expression for the variation of the velocity of sound with temperature is given and a fair estimate of the critical temperature is shown to be possible therefrom.

In recent years a number of investigators [1] have determined the velocity of sound in liquids particularly for the ultrasonic range of frequencies. Data for the velocity of sound in some liquids at different temperatures are also available.[2] All other liquids except water show a considerable increase in compressibility

TABLE I

Liquid.	Temperature °C.	Temperature Coefficient of acoustic velocity × 10³.	Temperature coefficient of volume expansion × 10³.	Ratio.
Benzene	15	−3·71	1·19	−3·12
	35	−3·68	1·24	−2·98
	45	−3·82	1·27	−3·00
Ether	15	−4·55	1·56	−2·92
Carbon tetra-chloride	15	−3·61	1·21	−2·99
	45	−3·55	1·26	−2·82
Heptane	25	−3·64	1·24	−2·93
	45	−3·89	1·29	−3·01
Octane	25	−3·52	1·12	−3·01
	45	−3·65	1·19	−3·05
Chlorobenzene	20	−2·79	0·89	−3·12
Aniline	25	−2·41	0·84	−2·87

with temperature, resulting in a decreased velocity of sound. Physical properties of a liquid like compressibility, density, etc., are intimately connected with the cohesive factor in van der Waal's equation being largely dependent on the internal forces between the molecules. According to Wheeler [3] it is possible to calculate the values of a number of properties of a liquid from a knowledge of the molecular volume at a given temperature and of the gaseous molecular attractive force constant and force coefficient, or alternatively of the parachor. Any simple relation between the velocity of sound and molecular volume of a liquid should therefore be interesting and fundamental.

A study of the measurements of the velocity of sound in liquids at various temperatures shows that the ratio of the temperature coefficient of acoustic velocity to the coefficient of volume expansion is constant for a number of liquids. Table I gives the values of the temperature coefficient of acoustic velocity, the coefficient of volume expansion, and their ratio for a number of liquids.

The mean value of the ratio is $-3 \pm 0 \cdot 12$

Thus

$$\frac{\frac{1}{v} \cdot \frac{dv}{dt}}{\frac{1}{V} \cdot \frac{dV}{dt}} = -3 \qquad \ldots \quad (1)$$

where v = velocity of sound in the liquid at temperature $t°C$.

V = volume of the liquid at the same temperature.

From the above result (1) empirically obtained, it follows

$$v^{\frac{1}{3}} . V = R \qquad \ldots \quad (2)$$

where R is a constant independent of the temperature of the liquid.[4] Table II gives the velocity of sound and density of the liquid at various temperatures. The variation of acoustic velocity with frequency (if any) is neglected and the liquids are assumed to have no acoustic dispersion. R, the product of the molecular volume V and $v^{\frac{1}{3}}$, is seen to be fairly constant over the entire temperature range for which values are available.

TABLE II

Liquid	Temperature °C	Velocity of sound m/sec.	Density.	R.
Benzene	10	1375	0·8896	975·7
	20	1324	0·8790	975
	30	1278	0·8684	975·4
	40	1231	0·8576	975·4
	50	1184	0·8467	975·2

TABLE II (*contd.*)

Liquid.	Temperature °C.	Velocity of Sound m./sec.	Density.	R.
Toluene	0	1414	0·8848	1168
	10	1370·5	0·8752	1168
	20	1327·5	0·8657	1169
	30	1284·5	0·8563	1169
	40	1242	0·8470	1168
	50	1199	0·8378	1168
Carbon tetra-chloride	0	1008	1·6327	944·3
	10	970	1·6134	944·1
	20	935	1·5939	943·4
	30	904	1·5748	944·3
	40	873·5	1·5557	945·0
	50	843	1·5361	945·8
Aniline	0	1742	1·0389	1077
	10	1700	1·0303	1078
	20	1659	1·0216	1077
	30	1619	1·0130	1078
	40	1579·5	1·0044	1079
	50	1540	0·9957	1079
Chlorobenzene	0	1362·5	1·1279	1106
	10	1322·5	1·1180	1105
	20	1284·5	1·1060	1106
	30	1248	1·0980	1104
	40	1212	1·0844	1106
	50	1178	1·0730	1108
Heptane	0	1235	0·7005	1533
	10	1196	0·6920	1536
	20	1154	0·6826	1538
	30	1112	0·6751	1536
	40	1070	0·6665	1536
	50	1028	0·6579	1536

TABLE II (*contd.*)

Liquid.	Temperature °C	Velocity of Sound m./sec.	Density.	R.
Octane	0	1277	0·7185	1724
	10	1235	0·7103	1724
	20	1192	0·7021	1723
	30	1150	0·6940	1722
	40	1108	0·6859	1721
	50	1066	0·6770	1719
Ether	0	1095	0·7362	1037
	10	1054	0·7248	1040
	20	1006	0·7135	1040
	30	949	0·7019	1037
Acetone	0	1273	0·8125	774·1
	10	1231	0·8014	776·4
	20	1190	0·7905	778·2
	30	1146	0·7788	780
	40	1102	0·7672	781·6
	50	1057	0·7554	782·9
Bromoform	10	953	2·886	862
	20	928	2·858	863·2
	30	907	2·830	864·8
	40	886	2·802	866·4
	50	865	2·774	868·4
Methyl alcohol	0	1187	0·8100	418·6
	10	1154	0·8007	419·5
	20	1121	0·7913	420·4
	30	1088	0·7818	421·3
	40	1056	0·7723	422·3
	50	1023·5	0·7627	423·1

TABLE II (*contd.*)

Liquid.	Temperature °C.	Velocity of Sound m./sec	Density.	R
Glycerine	10	1941·5	1·2671	906·5
	20	1923	1·2613	908
	30	1905	1·2553	909·3
	40	1886·5	1·2491	910·7
	50	1868·5	1·2427	912·2
Nitrotoluene	63	1373	1·116	1365
	67	1363	1·114	1365
	74	1335	1·105	1367
	95	1277	1·86	1370
	98	1267	1·083	1370
	123	1191	1·061	1370
	126	1176	1·058	1368
p-Dichlorobenzol.	72	1082	1·230	1227
	84	1050	1·219	1226
	94	983	1·208	1211
	150	837	1·142	1213

Since the molecular volume of a liquid is proportional to the cube of the inter-molecular distance it follows from the result $v^{\frac{1}{3}}.V = R$ that the velocity of sound in a liquid varies inversely as the ninth power of the distance between the molecules. According to Wheeler [5] the energy of a vibrating molecule is inversely proportional to the 10th power of the mutual distance between two molecular centres.

Hence $$E \propto \frac{1}{\sigma^{10}} \qquad \dots \quad (3)$$

From the empirical result we have obtained, it follows that

$$v \propto \frac{1}{\sigma^9}\,. \qquad \dots \quad (4)$$

Combining (3) and (4) it follows that

$$E \,/\, \frac{v}{} = \text{constant, independent of temperature.} \qquad (5)$$

According to Debye, the frequency of a vibrating molecule in a liquid is given by

$$\left(\frac{3N}{4\pi V}\right)^{1} \cdot v$$

where N = avogadro number,

V = molecular volume,

v = velocity of sound in the liquid.

Since $\frac{V}{N}$ is proportional to σ^3

we have

$$\nu = c\,\frac{v}{\ } \qquad \ldots \quad (6)$$

where c = constant.

Combining (5) and (6) we have

$$E \cdot = \text{constant}. \qquad (7)$$

This result shows that the energy of a vibrating molecule is proportional to its frequency.

VARIATION OF THE VELOCITY OF SOUND WITH TEMPERATURE

The equation, $v^{\frac{1}{3}}.V$ = constant, shows that the change in the velocity of sound with temperature is determined by the dependence of the density of the liquid on temperature. The variation of density[6] with temperature from the freezing point to the critical point is represented for non-associated liquids by the equation

$$D - d = D_0\left(1 - \frac{\theta}{\theta_c}\right)^{\frac{3}{10}}$$

where D = density of the liquid at $\theta°$ Abs.,

d = density of the vapour at $\theta°$ Abs.

The equation also holds good for associated liquids over the lower part of the temperature range and in some cases nearly to the critical point. The zero volume $\frac{1}{D_0}$ is nearly proportional to the critical volume for most of the liquids. Further, the critical temperature predicted from density observations are in good agreement with the observed values.

In the lower temperature range the density of the vapour is small and may be neglected in comparison with D and so we have

$$D = D_o\left(1 - \frac{\theta}{\theta_c}\right)^{\frac{3}{10}}.$$

Combining this with

$$\frac{v^{\frac{1}{3}}.M}{D} = \text{constant}.$$

we have

$$v = v_o\left(1 - \frac{\theta}{\theta_c}\right)^{\frac{3}{10}}.$$

This equation gives the variation of the velocity of sound with temperature. The critical temperatures deduced from sound velocity measurements are collected in Table III and are compared with the observed values. The agreement is satisfactory.

TABLE III

Liquid.	θ_c Cal.	θ_c Expt.
Benzene	546	561·5
Carbon tetrachloride	551	556·1
Chlorobenzene	607	632
Diethyl ether	477	467
Toluene	572	594
Octane	549	569
Heptane	543	540
Nitrotoluene	734	754
p-Dichlorobenzene	660	675

While considering the temperature variations of physical properties of a liquid, we have found it necessary to define a new characteristic temperature Θ given by $\frac{\theta_c - \theta}{\theta_c - \theta_f}$ where θ_c and θ_f refer respectively to the critical temperature and the melting point of the liquid. It has been shown that, expressed in terms of this characteristic temperature, many of the physical properties of the liquid vary with temperature according to a simple law[7]

$$Z = Z_f\,\Theta^n,$$

where Z_f = value of the physical entity, at the melting point θ_f
n = a positive or negative fraction.

In terms of this reduced temperature the variation of velocity of sound with emperature in particular is given by

$$v = v_f \, \Theta^{0 \cdot 9} \; .$$

In conclusion it gives me great pleasure to thank Mr. L. Sibaiya for his guidance during this investigation and Professor A. Venkat Rao Telang for his encouragement.

REFERENCES

[1] Freyer, Hubbard, Andrews, *J. Amer. Chem. Soc.*, **51**, 759 (1929); Parthsarathy, *Ind. Acad. Sci*, **2A**, 497 (1935); *Ind. Acad. Sci.*, **4A**, 59 (1936), *Ind. Acad. Sci.*, **3A**, 285, 297, 482 and 519; Schaafs, *Zeits. f. physik*, **106**, 658 (1937) and Swanson, *J. Chem. Phys.*, **2**, 689 (1934).

[2] Freyer Hubbard, Andrews, *J. Amer. Chem Soc*, **51**, 759 (1929); Schaafs, *Zeits. f. physik*, **106**, 658 (1937).

[3] Wheeler, *Trans. Nat. Inst. Sc. of India*, **1**, 333 (1938).

[4] M. Rama Rao, *Curr. Sci.*, **8**, 510, (1939).

[5] Wheeler *Trans. Nat. Inst. Sc. of India*, **1**, 333 (1938).

[6] Sugden, *J. Chem. Soc.*, 1780-86 (1927); *J. Chem. Soc.*, 1055 (1929).

[7] L. Sibaiya and M. Rama Rao. *Curr. Sci.*, **8**, 359 (1938).